

**PESTICIDE AND/OR PLANT GROWTH REGULATING COMPOSITIONS**DESCRIPTION

The present invention relates to pesticidal compositions and/or compositions which regulate the growth of insects and/or plants, which compositions contain specific dendrimers and which can be used in particular in the fields of agriculture and/or public or domestic hygiene; likewise, it relates to processes for the treatment and/or protection of crops and/or for public or domestic hygiene in which these compositions are employed; it also relates to processes for the preparation of such compositions or else to specific dendrimers.

A very large number of pesticidal compositions and/or compositions which regulate the growth of insects and/or plants are known, in particular through the French or European patents or patent applications EP-869 712, FR-2 733 502, EP-854 676, EP-851 729, EP-823 212 and the like.

The French, European or international documents, patents or patent applications WO-88/01179, FR-2 734 268, FR-2 761 601, EP-765 357, EP-736 059, EP-726 502 or the publication Synthesis No. 10, 997, pp. 1199-1207 described uses of dendrimers.

It is an object of the present invention to provide compositions which contain dendrimers which can form a gel in combination with a pesticidal active substance and/or an active substance which regulates the growth of plants and/or insects and which can be used in agriculture and/or in public or domestic hygiene, these compositions being in the form of a gel.

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It is an object of the present invention to provide compositions based on dendrimers which can form a gel

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and whose structure shows two types of insertion volume, in particular of active substance.

5 It is an object of the present invention to provide compositions based on dendrimers which can form a gel and whose structure comprises internal cavities which belong to the dendrimer molecules themselves and spaces which belong to the gel structure formed by said dendrimers.

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It is an object of the present invention to provide compositions whose active substance is in part localized in the internal cavities of the dendrimers used, while the remainder is localized in the structure of the gel formed by the said dendrimers.

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It is a complementary object of the present invention to provide compositions where at least half of the active substance is localized in the structure of the gel formed by the dendrimers used.

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The present invention relates to dendrimers with an improved capacity, in particular to dendrimers which can form a gel.

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Another object of the present invention is to provide pulverulent compositions based on a dendrimer which can form a gel and in combination with one or more pesticidal active substances and/or active substances which regulate the growth of plants and/or insects.

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It is an object of the present invention to provide gelled insecticidal compositions based on a dendrimer which can form a gel.

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It is an object of the present invention to provide gelled fungicidal compositions based on a dendrimer which can form a gel.

It is an object of the present invention to provide gelled herbicidal compositions based on a dendrimer which can form a gel.

- 5 It is an object of the present invention to provide gelled compositions which regulate the growth of insects and/or plants and which are based on a dendrimer which can form a gel.
- 10 It is a further object of the present invention to provide processes for the protection and/or treatment of crops in which the compositions according to the invention are employed.
- 15 It is another object of the present invention to provide compositions in pulverulent form which can be used in the fields of agriculture and/or public or domestic hygiene, where these pulverulent compositions can be stored over long periods without any
- 20 maintenance, while essentially maintaining their characteristics.

Likewise, it is an object of the present invention to provide protection and/or treatment methods which can

25 be used in public or domestic hygiene in which the compositions according to the invention, in particular insecticidal compositions and/or compositions which regulate the growth of insects and/or of pests, are employed.

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It is a complementary object of the present invention to provide insecticidal and/or nematocidal and/or acaricidal and/or rodenticidal baits.

- 35 These insecticidal and/or nematocidal and/or acaricidal and/or rodenticidal baits in the form of gelled compositions are likewise an object of the present invention.

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It is a supplementary object of the present invention to provide compositions which can be used in the fields of agriculture and/or public or domestic hygiene and which have an improved long-term stability, in particular when stored over long periods, and thus to allow the efficacy of the active substance used to be retained.

It is another object of the present invention to provide compositions whose handling risk is very much reduced owing to the fact that they are in gelled form.

Likewise, an object of the present invention relates to compositions in gelled form which can be used in the fields of agriculture and/or public or domestic hygiene and whose active substance is progressively released.

A complementary object of the present invention relates to compositions in gelled form which can be used in the fields of agriculture and/or public or domestic hygiene and whose active substance is released in a controlled manner.

It is another object of the present invention to provide compositions which, in addition to the above-mentioned advantages, present improved safety for the user and/or the environment, in particular compositions according to the invention in which one or more toxic active substances are employed.

It is another object of the present invention to provide processes for the preparation of compounds in gelled form which can be used in the fields of agriculture and/or public or domestic hygiene.

It is another object of the present invention to provide specific dendrimers which can form a gel.

Compositions according to the invention

It has now been found that these aims can be achieved fully or in part owing to the compositions according to the invention which can be used in particular in the fields of agriculture and/or public or domestic hygiene. These compositions according to the invention contain

- one or more active substances which can be used in particular in the fields of agriculture and/or public or domestic hygiene,
- one or more gellable dendrimers,
- a liquid mineral or organic carrier.

In the present text, active substance is understood as meaning any active substance which can be used in agriculture and/or in public or domestic hygiene, especially any pesticidal active substance and/or any active substance which regulates the growth of plants and/or of insects or pests.

The invention likewise relates to compositions according to the invention which contain mixtures, associations, combinations or any other form of formulation of more of these active substances, which will be the subject of a later development.

An essential aspect of the present invention is the use of specific dendrimers.

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The term dendrimer denotes polymers whose spatial structure is tree-like, whence the use of a prefix borrowed from the Greek language, which is derived from the term *dendro*, which means tree, to denote this family of polymeric macromolecules with a tree-like structure.

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Dendrimers which can be used for the compositions according to the invention are most particularly

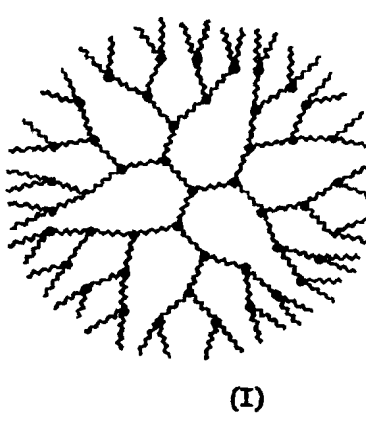
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macromolecules whose tree-like structure starts from a central part and extends in all directions.

The dendrimers employed in the compositions according to the invention are thus macromolecules composed of a central part, referred to as the core of the dendrimer, to which series of branched chains, referred to as dendrons, are attached.

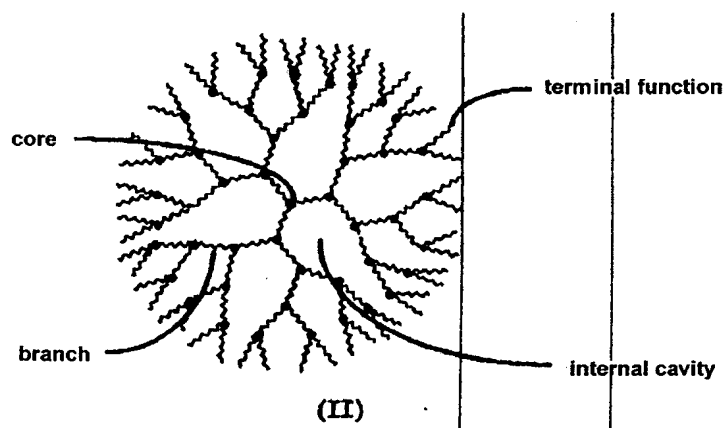
Figure (I) is a schematic representation of the tree-like structure of the type to which the dendrimers of the compositions according to the invention belong. This structure contains

- a core, which is most frequently composed of a multifunctional chemical group and capable of being attached to several branched chains, or dendrons;
- branches, generally composed of linear or branched organic moieties which are attached between each other and to the abovementioned core and which have a tree-like structure;
- chemical terminal functions, that is to say which form the outer end of these branches;
- internal cavities which result inherently from the branchings of these branches.



The schematic representation of Figure (II) refers back to Figure (I) and is complemented by a key, thus allowing a more precise illustration of the elements of

which the tree-like structure of the type of the structure of the dendrimers according to the invention may be composed of.



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The organic core is thus the central part of the dendrimers which can be used for the compositions according to the invention. In general, it is composed of a chemical group, most frequently an organic polyfunctional chemical group which can be attached to a plurality of branched chains. The core of the dendrimers of the present invention is likewise characterized by a multiple valency which corresponds to the number of dendrons to which it can be attached. Details regarding the core of these dendrimers which are employed in the compositions according to the invention will be given in the present text when the said dendrimers are described in detail.

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The dendrons of the said dendrimers are organic branched chains which are attached to the core. In general, these dendrons are series of these branched chains.

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The terminal functions of the dendrimers which can be used for the compositions according to the invention are chemical functions which are present at the ends of the dendrons; among the very large number of chemical functions which the said terminal functions can consist

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of, the ammonium, amidinium, pyridinium, guanidinium, carboxylate or else carboxylic acid functions may be mentioned by way of example. These terminal functions usually impart some of their characteristics to them, in particular the possibility of a very large number of individual reactions at the periphery.

The internal cavities of the dendrimers employed in the compositions according to the invention are inherently the result of the fact that branchings of these dendrimers exist. These internal cavities allow in particular the inclusion of various substances in the centre of the tree-like structure of the said dendrimers. However, the size and accessibility of these internal cavities limits the inclusion of the said substances to only those molecules whose size and characteristics are compatible therewith.

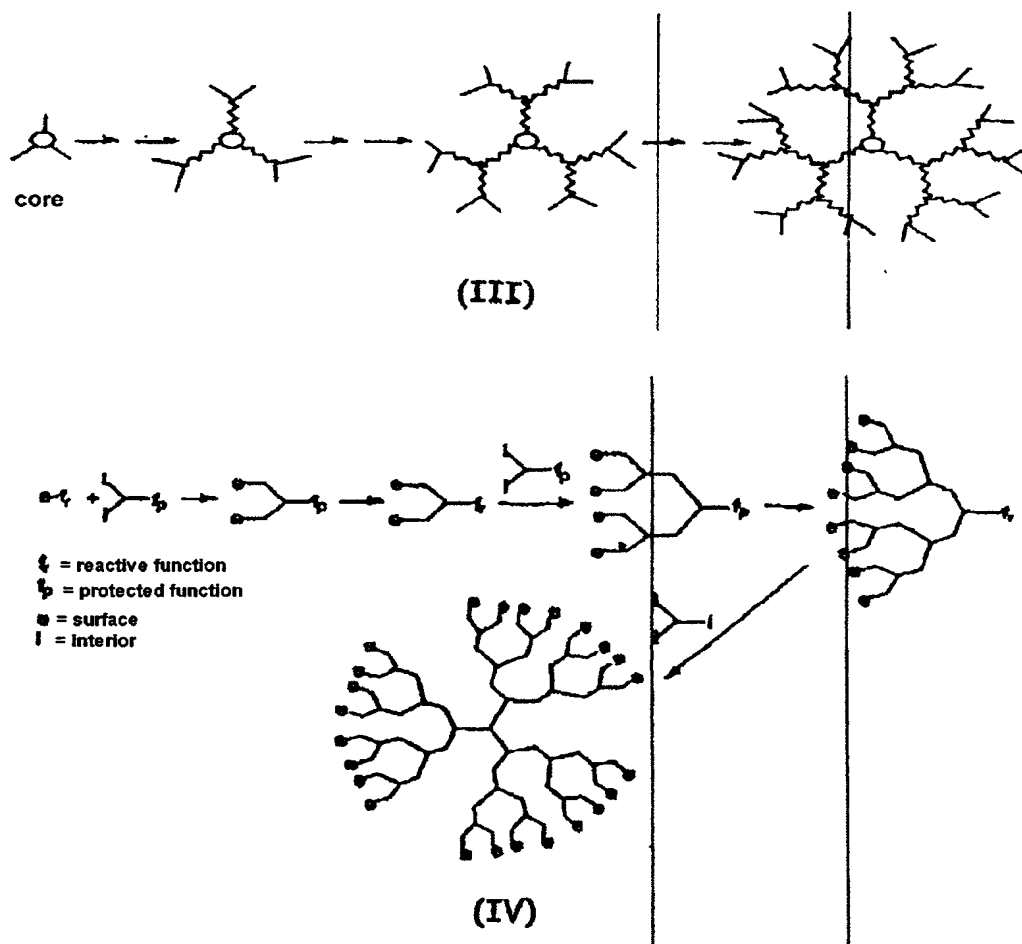
In principle, two types of synthetic methods, namely the divergent syntheses and the convergent syntheses may be mentioned for the preparation of dendrimers which can be used for the compositions of the present invention:

- in the divergent methods the synthesis progresses from the core towards the periphery by grafting increasing numbers of small molecules onto the surface of the dendrimer, which have a large number of chemical functions; such a synthetic pathway is shown in Scheme (III);

- in the convergent methods the synthesis progresses from the periphery towards the core by associating increasingly large molecules, which permanently have available a chemical function at the core, with each other; such a synthetic pathway is shown in Scheme (IV).



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5 With these construction methods all of the branch points of the branches located at a similar distance from the core of the dendrimers employed in the compositions according to the invention can moreover be defined as forming part of the same generation, and  
 10 each generation can thus define layers which are composed of these branch points for the said dendrimers.

Moreover, this way of constructing dendrimers by  
 15 repeating steps is advantageous in as far as it can allow precise control of their molecular weight, their size, their shape and their ability to react chemically, inter alia.

20 Various texts of the work Les dendrimères [The dendrimers] of the ECRIN group, which was published in

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June 1998 by éditions SACER, in which dendrimers are described, may be referred to.

5 The compositions according to the invention are characterized in that they contain an active substance as defined above, a dendrimer which can form a gel, and a mineral or organic liquid carrier.

10 Moreover, and depending on the type of disease to be treated, the type of harmful plants, insects and/or pests to be controlled, killed or eradicated, or depending on the level of infestation with these pests, or else on the climatic conditions and/or the soil conditions, the compositions according to the invention  
15 can contain any other substance conventionally used in the formulation of compositions which can be used in the fields of agriculture and/or public or domestic hygiene.

20 Among these compounds the following may be mentioned by way of example in particular: adjuvants, anti-caking agents, colorants, thickeners, surfactants, antifoams, detergents such as salts of alkaline earth metals, dispersants, alkalinizing agents such as bases,  
25 stickers, emulsifiers, oxidants such as free-radical scavengers or anti-hydroperoxide catalysts, corrosion inhibitors, attractants and/or food substances for the preparation of insecticidal baits.

30 More generally, the compositions according to the invention can contain any solid or liquid additives which are conventionally used in the art of formulation and acceptable for use in, for example, in agriculture and/or public or domestic hygiene.

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The compositions according to the invention may contain one or more associated active substances of the fungicide and/or insecticide and/or acaricide and/or rodenticide and/or nematocide and/or insect repellent

and/or pest repellent and/or plant growth regulator and/or insect growth regulator type and/or one or more herbicidal active substances, likewise depending on the type of diseases to be treated, the type of harmful plants, insects and/or pests to be controlled, killed or eradicated, or depending on the level of infestation with these pests, or else on the climatic conditions and/or the soil conditions.

10 In general, the pesticidal active substances and/or growth-regulatory active substances which can be used in the formulation of the compositions according to the invention are those listed in any work on crop protection, for example the "Index Phytosanitaire" [Crop  
15 Protection Index] (which is published by the A.C.T.A., Direction technique de l'Association de Coordination Technique Agricole) or else The Pesticide Manual (of the British Crop Protection Council, edited by Clive Tomlin) or else The Electronic Pesticide Manual version  
20 1.1 (of the British Crop Protection Council, edited by Clive Tomlin).

The following may be mentioned by preference among the fungicidal active substances which can be used alone or  
25 in association with other active substances, in particular pesticides, in the compositions according to the invention: 2-phenylphenol, 8-hydroxyquinoline sulfate, AC 382042, Ampelomyces quisqualis, azaconazole, azoxystrobin, Bacillus subtilis,  
30 benalaxyl, benomyl, biphenyl, bitertanol, blasticidin S, Bordeaux mixture, borax, bromuconazole, bupirimate, calboxin, calcium polysulfide, captafol, captan, carbendazim, carpropamid (KTU 3616), CGA 279202, quinomethionate, chlorothalonil, chlozolate, copper hydroxide, copper naphthenate, copper  
35 oxychloride, copper sulfate, copper(I) oxide, cymoxanil, cyproconazole, cyprodinil, dazomet, debacarb, dichlofluanid, dichlomezine, dichlorophen, diclocymet, dicloran, diethofencarb, difenoconazole,

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difenzoquat, difenzoquat-methylsulfate, diflumetorim,  
 dimethirimol, dimethomorph, diniconazole,  
 diniconazole-M, dinobuton, dinocap, diphenylamine,  
 dithianon, dodemorph, dodemorph acetate, dodine, dodine  
 5 (free base), edifenphos, epoxiconazole (BAS 480F),  
 ethasulfocarb, ethirimol, etridiazole, famoxadone,  
 fenamidone, fenarimol, fenbuconazole, fenfin, fenfuram,  
 fenhexamid, fencpiclonil, fenpropidin, fenpropimorph,  
 fentin acetate, fentin hydroxide, ferbam, ferimzone,  
 10 fluazinam, fludioxonil, fluoroimide, fluquinconazole,  
 flusilazole, flusulfamide, flutolanil, flutriafol,  
 folpet, formaldehyde, fosetyl, fosetyl-aluminium,  
 fuberidazole, furalaxyl, Fusarium oxysporum,  
 Gliocladium virens, guazatine, guazatine acetates,  
 15 GY-81, hexachlorobenzene, hexaconazole, hymexazol,  
 ICIA0858, IKF-916, imazalil, imazalil sulfate,  
 imibenconazole, iminoctadine, iminoctadine triacetate,  
 iminoctadine tris(albesilate), ipconazole, iprobenfos,  
 iprodione, iprovalicarb, kasugamycin, kasugamycin  
 20 hydrochloride hydrate, kresoxim-methyl, mancopper,  
 mancozeb, maneb, mepanipyrim, mepronil, mercury(II)  
 chloride, mercury(II) oxide, mercury(I) chloride,  
 metalaxyl, metalaxyl-M, metam, metam-sodium,  
 metconazole, methasulfocarb, methyl isothiocyanate,  
 25 metiram, metominostrobin (SSF-126), MON65500,  
 myclotbutanil, nabam, naphthenic acid, natamycin,  
 nickel bis(dimethyldithiocarbamate), nitrothal-  
 isopropyl, nuarimol, octhilinone, ofurace, oleic acid  
 (the fatty acids), oxadixyl, oxine-copper, oxycarboxin,  
 30 penconazole, pencycuron, pentachlorophenol,  
 pentachlorophenyl laurate, perfurazoate, phenylmercury  
 acetate, Phlebiopsis gigantea, phthalide, piperalin,  
 polyoxine B, the polyoxines, polyoxorim, potassium  
 hydroxyquinolinesulfate, probenazole, prochloraz,  
 35 procymidone, propamocarb, propamocarb hydrochloride,  
 propiconazole, propineb, pyrazophos, pyributicarb,  
 pyrifenox, pyrimethanil, pyroquilon, quinoxifen,  
 quintozone, RH-7281, sec-butylamine, sodium  
 2-phenylphenoxide, spiroxamine (KWG 4168), Streptomyces

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griseoviridis, sulfur, tar oils, tebuconazole, tecnazene, tetraconazole, thiabendazole, thifluzamide, thiophanate-methyl, thiram, tolclofos-methyl tolylfluand, triadimefon, triadimenol, triazoxide, 5 Trichoderma harzianum, tricyclazole, tridemorph, triflumizole, triforine, triticonazole, validamycin, vinclozolin, zinc naphthenate, zineb, ziram, the compounds with the chemical name methyl (E,E)-2-(2-(1-(1-(2-pyridyl)propyloxyimino)-1-cyclopropylmethyloxy- 10 methyl)phenyl)-3-ethoxypropenoate and 3-(3,5-dichlorophenyl)-4-chloropyrazole.

The following may be mentioned among the insecticidal, acaricidal and nematocidal active substances which can 15 be used in the compositions according to the invention, either alone or in association with other active substances, in particular pesticides: abamectin, acephate, acetamiprid, oleic acid, acrinathrin, aldicarb, alanycarb, allethrin [(1R)-isomers], 20  $\alpha$ -cypermethrin, amitraz, avermectin B1 and its derivatives, azadirachtin, azamethiphos, azinphos-ethyl, azinphos-methyl, Bacillus thurigiensis, bendiocarb, benfuracarb, bensultap,  $\beta$ -cyfluthrin,  $\beta$ -cypermethrin, bifenazate, bifenthrin, bioallethrin, 25 bioallethrin (S-cyclopentenyl isomer), bioresmethrin, borax, buprofezin, butocarboxim, butoxycarboxim, piperonyl butoxide, cadusafos, carbaryl, carbofuran, carbosulfan, cartap, cartap hydrochloride, chlordane, chlorethoxyfos, chlorfenapyr, chlorfenvinphos, 30 chlorfluazuron, chlormephos, chloropicrin, chlorpyrifos, chlorpyrifos-methyl, mercury(I) chloride, coumaphos, cryolite, cryomazine, cyanophos, calcium cyanide, sodium cyanide, cycloprothrin, cyfluthrin, cyhalothrin, cypermethrin, cyphenothrin [(1R)-trans 35 isomers], dazomet, DDT, deltamethrin, demeton-S-methyl, diafenthiuron, diazinon, ethylene dibromide, ethylene dichloride, dichlorvos, dicofol, dicrotophos, diflubenzuron, dimethoate, dimethylvinphos, diofenolan, disulfoton, DNOC, DPX-JW062 and DP, empenthrin [(EZ)-

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(1R) isomers]: endosulfan, ENT 8184, EPN, esfenvalerate, ethiofencarb, ethion, ethiprole, chemical name: 5-amino-3-cyano-1-(2,6-dichloro-4-trifluoromethylphenyl)-4-ethylsulfinylpyrazole,

5 ethoprophos, etofenprox, etoxazole, etrimfos, famphur, fenamiphos, fenitrothion, fenobucarb, fenoxycarb, fenpropathrin, fenthion, fenvalerate, fipronil and the compounds of the arylpyrazole family, flucycloxuron, flucythrinate, flufenoxuron, flufenprox, flumethrin,

10 fluofenprox, sodium fluoride, sulfuryl fluoride, fonofos, formetanate, formetanate hydrochloride, formothion, furathiocarb, gamma-HCH, GY-81, halofenozide, heptachlor, heptenophos, hexaflumuron, sodium hexafluorosilicate, tar oils, petroleum oils,

15 hydramethylnon, hydrogen cyanide, hydroprene, imidacloprid, imiprothrin, indoxacarb, isazofos, isofenphos, isoprocarb, methyl isothiocyanate, isoxathion, lambda-cyhalothrin, pentachlorophenyl laurate, lufenuron, malathion, MB-599, mecarbam,

20 methacrifos, methamidophos, methidathion, methiocarb, methomyl, methoprene, methoxychlor, metolcarb, mevinphos, milbemectin and its derivatives, monocrotophos, naled, nicotine, nitenpyram, nithiazine, novaluron, omethoate, oxamyl, oxydemeton-methyl,

25 Paecilomyces fumosoroseus, parathion, parathion-methyl, pentachlorophenol, sodium pentachlorophenoxide, permethin, phenothrin [(1R)-trans isomer], phenthoate, phorate, phosalone, phosmet, phosphamidon, phosphine, aluminium phosphide, magnesium phosphide, zinc

30 phosphide, phoxim, pirimicarb, pirimiphos-ethyl, pirimiphos-methyl, calcium polysulfoxide, prallethrin, profenafos, propaphos, propetamphos, propoxur, prothiofos, pyraclofos, pyrethrins (chrysanthemates, pyrethrates, pyrethrum), pyretrozine, pyridaben,

35 pyridaphenthion, pyrimidifen, pyriproxyfen, quinalphos, resmethrin, RH-2485, rotenone, RU 15525, silafluofen, sulcofuron-sodium, sulfotep, sulfuramide, sulprofos, Tau-fluvalinate, tebufenozide, tebupirimfos, teflubenzuron, tefluthrin, temephos, terbufos,

tetrachlorvinphos, tetramethrin, tetramethrin [(1R) isomers],  $\theta$ -cypermethrin, thiametoxam, thiocyclam, thiocyclam hydrogen oxalate, thiodicarb, thiofanox, thiometon, tralomethrin, transfluthrin, triazamate, triazophos, trichlorfon, triflumuron, trimethacarb, vamidothion, XDE-105, XMC, xylycarb, zeta-cypermethrin, ZXI 8901, the compound with the chemical name 3-acetyl-5-amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinylpyrazole.

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Among the herbicidal active substances which can be used in the compositions according to the invention, alone or in association with other active substances, in particular pesticides, the following may be mentioned: 2,3,6-TBA, 2,4-D, 2,4-D-2-ethylhexyl, 2,4-DB, 2,4-DB-butyl, 2,4-DB-dimethylammonium, 2,4-DB-isooctyl, 2,4-DB-potassium, 2,4-DB-sodium, 2,4-D-butotyl (2,4-D-butotyl(2,4-D-butoxyethyl ester)), 2,4-D-butyl, 2,4-D-dimethylammonium, 2,4-D-diolamine, 2,4-D-isooctyl, 2,4-D-isopropyl, 2,4-D-sodium, 2,4-D-trolamine, acetochlor, acifluorfen, acifluorfen-sodium, aclonifen, acrolein, AKH-7088, alachlor, alloxydim, alloxydim-sodium, ametryn, amidosulfuron, amitrole, ammonium sulfamate, anilofos, asulam, asulam-sodium, atrazine, azafenidin, azimsulfuron, benazolin, benazolin-ethyl, benfluralin, benfuresate, benoxacor, bensulfuron, bensulfuron-methyl, bensulide, bentazone, bentazone-sodium, benzofenap, bifenox, bilanafos, bilanafos-sodium, bispyribac-sodium, borax, bromacil, bromobutide, bromofenoxim, bromoxynil, bromoxynil-heptanoate, bromoxynil-octanoate, bromoxynil-potassium, butachlor, butamifos, butralin, butroxydim, butylate, cafenstrole, carbetamide, carfentrazone-ethyl, chlomethoxyfen, chloramben, chlorbromuron, chloridazon, chlorimuron, chlorimuron-ethyl, chloroacetic acid, chlorotoluron, chlorpropham, chlorsulfuron, chlorthal, chlorthal-dimethyl, chlorthiamid, cinmethylin, cinosulfuron, clethodim, clodinafop, clodinafop-propargyl, clomazone, clomeprop, clopyralid,

clopyralid-olamine, cloquintocet, cloquintocet-mexyl,  
 cloransulam-methyl, CPA, CPA-dimethylammonium,  
 CPA-isooctyl, CPA-thioethyl, cyanamide, cyanazine,  
 cycloate, cyclosulfamuron, cycloxydim, cyhalofop-butyl,  
 5 daimuron, dalapon, dalapon-sodium, dazomet,  
 desmedipham, desmetryn, dicamba, dicamba-  
 dimethylammonium, dicamba-potassium, dicamba-sodium,  
 dicamba-trolamine, dichlobenil, dichlormid,  
 dichlorprop, dichlorprop-butotyl (dichlorprop-butotyl  
 10 (dichlorprop butoxyethyl ester)), dichlorprop-  
 dimethylammonium, dichlorprop-isooctyl, dichlorprop-P,  
 dichlorprop-potassium, diclofop, diclofop-methyl,  
 difenzoquat, difenzoquat-methylsulfate, diflufenican,  
 diflufenzopyr (BAS 654 OO H), dimefuron, dimepiperate,  
 15 dimethachlor, dimethametryn, dimethenamid, dimethipin,  
 dimethylarsinic acid, dinitramine, dinoterb, dinoterb  
 acetate, dinoterb-ammonium, dinoterb-diolamine,  
 diphenamid, diquat, diquat dibromide, dithiopyr,  
 diuron, DNOC, DSMA, endothal, EPTC, esprocarb,  
 20 ethalfluralin, ethametsulfuron-methyl, ethofumesate,  
 ethoxysulfuron, etobenzanid, fenchlorazole-ethyl,  
 fenclorim, fenoxaprop-P, fenoxaprop-P-ethyl, fenuron,  
 fenuron-TCA, ferrous sulfate, flamprop-M, flamprop-M-  
 isopropyl, flamprop-M-methyl, flazasulfuron, fluazifop,  
 25 fluazifop-butyl, fluazifop-P, fluazifop-P-butyl,  
 fluazolate, fluchloralin, flufenacet (BAS FOE 5043),  
 flumetsulam, flumiclorac, flumiclorac-pentyl,  
 flumioxazin, fluometuron, fluoroglycofen,  
 fluoroglycofen-ethyl, flupaxam, flupoxam, flupropanate,  
 30 flupropanate-sodium, flupyr-sulfuron-methyl-sodium,  
 flurazole, flurenol, flurenol-butyl, fluridone,  
 flurochloridone, fluroxypyr, fluroxypyr-2-butoxy-1-  
 methylethyl, fluroxypyr-methyl, flurtamone,  
 fluthiacet-methyl, fluxofenim, fomesafen, fomesafen-  
 35 sodium, fosamine, fosamine-ammonium, furilazole,  
 glyphosate, glufosinate, glufosinate-ammonium,  
 glyphosate-ammonium, glyphosate-isopropylammonium,  
 glyphosate-sodium, glyphosate-trimesium, halosulfuron,  
 halosulfuron-methyl, haloxyfop, haloxy-P-methyl,



haloxyfop-etotyl, haloxyfop-methyl, hexazinone,  
 hilanafos, imazacluin, imazamethabenz, imazamox,  
 imazapyr, imazapyr-isopropylammonium, imazaquin,  
 imazaquin-ammonium, imazamethabenz-methyl, imazethapyr,  
 5 imazethapyr-ammonium, imazosulfuron, imizapic (AC  
 263,222), indanofan, ioxynil, ioxynil octanoate,  
 ioxynil-sodium, isoproturon, isouron, isoxaben,  
 isoxaflutole, lactofen, laxynel octanoate, laxynil-  
 sodium, lenacil, linuron, MCPA, MCPA-butotyl, MCPA-  
 10 dimethylammonium, MCPA-isooctyl, MCPA-potassium, MCPA-  
 sodium, MCPA-thioethyl, MCPB, MCPB-ethyl, MCPB-sodium,  
 mecoprop, mecoprop-P, mefenacet, mefenpyr-diethyl,  
 mefluidide, mesulfuron-methyl, metam, metamitron,  
 metam-sodium, metezachlor, methabenzthiazuron, methyl  
 15 isothiocyanate, methylarsonic acid, methyldymron,  
 metobenzuron, metobromuron, metolachlor, metosulam,  
 metoxuron, metribuzin, metsulfuron, molinate,  
 monolinuron, MPB-sodium, MSMA, napropamide, naptalam,  
 naptalam-sodium, neburon, nicosulfuron, nonanoic acid,  
 20 norflurazon, oleic acid (fatty acids), orbencarb,  
 oryzalin, oxabetrinil, oxadiargyl, oxasulfuron,  
 oxodiazon, oxyfluorfen, paraquat, paraquat dichloride,  
 pebulate, pendimethalin, pentachlorophenol,  
 pentachlorophenyl laurate, pentanochlor, pentoxazone,  
 25 petroleum oils, phenmedipham, picloram, picloram-  
 potassium, piperophos, pretilachlor, primisulfuron,  
 primisulfuron-methyl, prodiamine, prometon, prometryn,  
 propachlor, propanil, propaquizafop, propazine,  
 propham, propisochlor, propyzamide, prosulfocarb,  
 30 prosulfuron, pyraflufen-ethyl, pyrazasulfuron,  
 pyrazolynate, pyrazosulfuron-ethyl, pyrazoxyfen,  
 pyribenzoxim, pyributicarb, pyridate, pyriminobac-  
 methyl, pyriothiobac-sodium, quinclorac, quinmerac,  
 quinofoamine, quizalofop, quizalofop-ethyl,  
 35 quizalofop-P, quizalofop-P-ethyl, quizalofop-P-  
 terfuryl, rimsulfuron, sethoxydim, siduron, simazine,  
 simetryn, sodium chlorate, sodium chloroacetate, sodium  
 pentachlorophenoxide, sodium dimethylarsinate,  
 sulcotrione, sulfentrazone, sulfometuron, sulfometuron-

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methyl, sulfosulfuron, sulfuric acid, tars, TCA-sodium, tebutam, tebuthiuron, tepraluxydim (BAS 62OH), terbacil, terbumeton, terbuthylazine, terbutryn, thenylchlor, thiazopyr, thifensulfuron, thifensulfuron-methyl, thiobencarb, thiocarbazon, tralkoxydim, tri-allate, triasulfuron, triaziflam, tribenuron, tribenuron-methyl, trichloroacetic acid, triclopyr, triclopyr-butotyl, triclopyr-triethylammonium, trietazine, trifluralin, triflusulfuron, triflusulfuron-methyl, vernolate, YRC 2388.

In the compositions according to the invention, the active substance(s) may be present in different physical forms, in particular in solid form, but also in liquid or semi-liquid form.

The active substance(s) of the compositions according to the invention are present in amounts of between 0.5 and 99.99%, preferably between 5 and 70% by weight of the said compositions.

The dendrimers employed in the compositions according to the invention, also referred to as dendrimers according to the invention, are those dendrimers which can form a gel.

An advantageous method for finding out if a particular dendrimer can form a gel consists in mixing the said dendrimer with water in weight ratios of 1.5/98.5, respectively, at a temperature of approximately 65°C; the mixture forms a gel in the sense of the present invention if, after 48 hours, the product obtained does not run when placed on a plane surface as a cubic mass.

In accordance with another method for finding out if a particular dendrimer can form a gel in a particularly advantageous quality for the invention, the said dendrimer is mixed at ambient temperature with water in weight ratios of 1/1 respectively; the mixture forms a

gel in the sense of the present invention if, after two weeks, the product obtained does not run when placed on a plane surface as a cubic mass.

5 Another method which is particularly advantageous for determining if a particular dendrimer can form a gel can consist of the following procedure: the dendrimer in question is mixed with water, preferably solubilized in water, in weight ratios of 1.8/98.2, respectively,  
10 at a temperature which may be between 40 and 65°C, and this mixture is then heated for 4 weeks at a temperature of approximately 60-65°C, whereby a gelled product is obtained which does not run when placed on a plane surface as a cubic mass.

15 In accordance with another aspect of the invention, the gels which can be formed by the dendrimers in question and which can be used for the compositions according to the invention are colloids with an essentially  
20 continuous phase which give a viscous jelly-like product; the system may also take the form of a dispersed system which consists for example of a high-molecular-weight compound or an aggregate of molecules of dendrimers which can be used for the compositions  
25 according to the invention in close association with a liquid mineral or organic carrier.

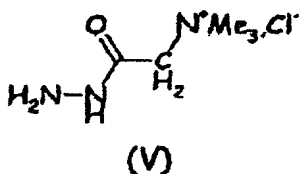
The dendrimers which can be used in accordance with the compositions of the invention and which are thus  
30 dendrimers which can form a gel can in particular be neutral dendrimers or dendrimers of the ionic type, either of the anionic or cationic type.

Neutral dendrimers which can be used in accordance with  
35 the compositions of the invention and which may be mentioned are those whose terminal functions are mainly composed of groups of the carboxylic acid type and/or phosphonic acid type and/or the sulphonic acid, sulphonate or sulphate type and/or of the amine type.

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Dendrimers of the ionic type which can be used in accordance with the compositions of the invention and which may be mentioned advantageously are the dendrimers whose terminal functions contain essentially groups selected from among the carboxylate and/or sulphonium and/or phosphonium and/or amidinium and/or guanidinium and/or ammonium groups, for example groups of the secondary, tertiary or quaternary ammonium type, very particularly groups of the pyridinium type.

Very particularly advantageous dendrimers which can be used for the compositions according to the invention and which may be mentioned are those particular dendrimers whose terminal functions contain essentially radicals derived from groups of the N-hydrazinoyl-carbonylmethyl-N,N,N-trialkylammonium halide type, among which groups for example N-hydrazinoylcarbonylmethyl-N,N,N-tri(n-propyl)ammonium chloride, which is referred to as Girard PR reactant, or N-hydrazinoylcarbonylmethyl-N,N,N-trimethylammonium chloride, which is shown in Figure (V) hereinbelow and which will be referred to as Girard T reactant throughout the following text may be mentioned, or else N-hydrazinoylcarbonylmethyl-N,N,N-pyridinium chloride, referred to as Girard P reactant throughout the following text may also be mentioned.



What are known as terminal functions of dendrimers which can be used in accordance with the compositions of the invention are attached at the ends of the branched chains which make up the branches of these dendrimers, either directly or by means of an organo-chemical residue referred to as connecting member in the present context.

What is known as the connecting member of the dendrimers which can be used for the compositions of the invention is most frequently composed of a hydrocarbon radical containing 2 to 50 carbon atoms, preferably 4 to 20 carbon atoms, it being possible for this radical to be saturated or unsaturated and/or linear or branched and/or substituted or unsubstituted.

What is known as the connecting member can likewise be composed of a hydrocarbon radical as defined above which contains in addition to carbon atoms one or more hetero atoms, in particular oxygen, sulphur, nitrogen, phosphorus or halogens.

The following groups may be mentioned as connecting members which can be used for the dendrimers employed in the compositions according to the invention: groups of the alkyl, aryl, alkoxyalkyl, alkoxyaryl, alkylhydrazinoyl, arylhydrazinoyl, carboxyalkylhydrazido, in particular carboxymethylhydrazido, cyanoalkyl, allyl, propargyl, halocycloalkyl, haloalkoxyalkyl, alkylthioalkyl, haloalkylthioalkyl, aminoalkyl, N-alkylaminoalkyl, N,N-dialkylaminoalkyl, acylaminoalkyl, arylalkyl, phenyliminoalkyl, iminoaryl, imidoalkyl, amidoaryl, phosphoalkyl, phosphoryl, thiophosphoryl, phosphoraminoalkyl, phosphoraminoaryl, phosphoriminoalkyl, phosphoriminoaryl, phosphorimidoalkyl, phosphorimidoaryl, hydrazinoalkyl, hydrazinoaryl, allylidenealkylhydrazino, allylidenearylhydrazino, epoxybenzylidene, dialkylphosphorimido, diarylphosphorimido, thioimidophosphoryl, thio-N-alkylazophosphoryl, thio-N-arylazophosphoryl which are optionally substituted by one or more groups selected from the groups of the hydroxyl, mercapto, nitro, thiocyanato, azido, cyano, pentafluorosulphonyl, alkyl, aryl, haloalkyl, alkoxy, haloalkoxy, alkylthio, haloalkylthio, alkoxyalkyl, haloalkoxyalkyl, alkylthioalkyl, haloalkylthioalkyl, cyanoalkyl, cyanoalkoxy, cyanoalkylthio, alkylsulphinyl, haloalkylsulphinyl,

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alkylsulphonyl, haloalkylsulphonyl and alkoxy sulphonyl, cycloalkyl, alkenyl, alkynyl, alkenyloxy, alkynyloxy, alkenylthio, alkynylthio, amino, N-alkylamino, N,N-dialkylamino, acylamino, hydroxyl, alkoxy, carboxy, carbamoyl, N-alkylcarbamoyl, N,N-dialkylcarbamoyl, alkoxy carbonyl and acyl.

The dendrimers employed in the compositions according to the invention preferably have bonds between atoms of the fifteenth column of the Periodic Table, this fifteenth column containing nitrogen as the first element and bismuth as the last element. More preferably, these dendrimers have bonds between phosphorus atoms and nitrogen atoms.

These bonds between atoms of the fifteenth column of the Periodic Table can be present in the dendrimers which can be used for the compositions according to the invention in amounts of from a few units to several thousand, indeed several tens of thousands, owing to the large size which these dendrimers can attain; for example, the number of these bonds can be between 2 and 80 000, preferably between 20 and 20 000.

As defined above, the organic core of the dendrimers which can be used for the compositions according to the invention is most frequently composed of a polyfunctional organochemical group which can be attached to a multiplicity of branched chains.

This core can likewise be characterized by a multiple valency which corresponds to the number of dendrons to which it can be attached directly in order to give a what is known as first-generation dendrimer.

The core of the dendrimers used within the scope of the invention preferably has a valency of between 2 and 20, by preference between 3 and 10. Thus, the dendrimers according to the invention, which are known as first-

generation dendrimers, can be attached to a number of dendrons of up to 20, by preference up to 10.

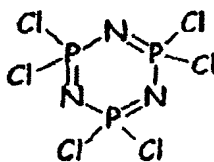
Most frequently, the core of the dendrimers according to the compositions of the invention is composed of a more or less complex radical or chemical group; it may be a hydrocarbon radical which generally contains 1 to 30 atoms and this hydrocarbon radical can be straight-chain, branched or cyclic, indeed polycyclic, and/or saturated or unsaturated and/or substituted or unsubstituted.

The core of the dendrimers employed in the compositions according to the invention is usually composed of a hydrocarbon radical containing one or more hetero atoms, in particular oxygen, sulphur, nitrogen, phosphorus or else halogens, in particular chlorine. If appropriate and by way of preference, the core of the dendrimers according to the invention contains up to 100% in terms of number of atoms of these hetero atoms.

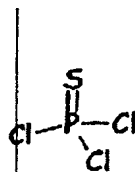
Examples which may be mentioned of precursors of radicals with hetero atoms which can be used as core of the dendrimers according to the invention are hexachlorocyclotriphosphazene or else trichlorothiophosphane; the chemical structure of these two compounds is shown hereinbelow in Figures (VI) and (VII).

Precursors are understood as meaning compounds which can precede the formation or preparation of radicals which can be used as core of the dendrimers according to the invention.

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(VI)



(VII)

As defined further above, the branches, or dendrons, of the dendrimers according to the invention are most frequently composed of branched organic chains which are attached to the core of these dendrimers.

These branched organic chains are usually composed of more or less complex hydrocarbon radicals, which can likewise contain a number of hetero atoms such as oxygen, sulphur, nitrogen, phosphorus or else the halogens, in particular chlorine.

In general, these dendrons are series of such branched chains, in other words the dendrimers according to the invention have most frequently dendrons which are composed of branched chains which have chemical motifs which are partly identical with, or similar to, each other.

The dendrimers which can be used within the scope of the present invention can have a large number of dendrons, and the number of these identical or similar chemical motifs is highly variable. Usually, the dendrimers according to the compositions of the invention have dendrons which are composed of a series of branched chains which contain chemical motifs among which 10%, preferably 20%, of the total number of chemical motifs are identical with, or similar to, each other. In other words, the dendrons of the dendrimers used in the invention can be composed of chemical motifs of which 9/10, preferably 4/5, differ from each other.



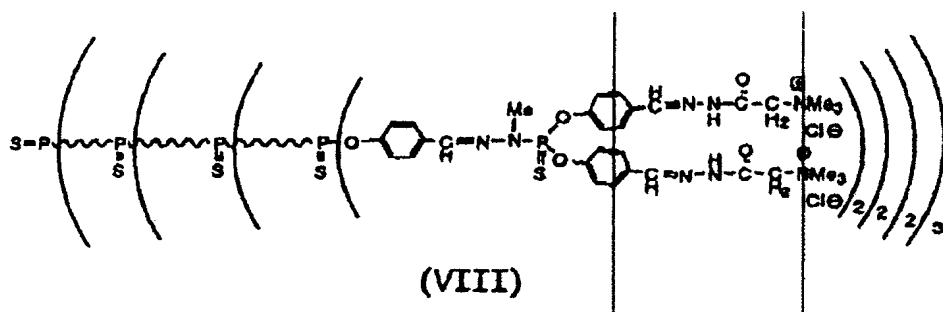
These chemical motifs which the dendrons of the dendrimers used for the compositions according to the invention are composed of can be chosen for example from among the groups of the alkyl, aryl, alkoxyalkyl, alkoxyaryl, alkylhydrazino, arylhydrazino, carboxy-alkylhydrazido and in particular carboxymethylhydrazido, cyanoalkyl, allyl, propargyl, halocycloalkyl, haloalkoxyalkyl, alkylthioalkyl, haloalkylthioalkyl, aminoalkyl, N-alkylaminoalkyl, N,N-dialkylaminoalkyl, acylaminoalkyl, arylalkyl, phenyliminoalkyl, iminoaryl, imidoalkyl, amidoaryl, phosphoralkyl, phosphoryl, thiophosphoryl, phosphoraminoalkyl, phosphoraminoaryl, phosphoriminoalkyl, phosphoriminoaryl, phosphorimidoalkyl, phosphorimidoaryl, hydrazinoalkyl, hydrazinoaryl, allylidenealkylhydrazino, allylidenearylhylhydrazino, epoxybenzylidene, dialkylphosphorimido, diarylphosphorimido, thioimido-phosphoryl, thio-N-alkylazophosphoryl or thio-N-arylazophosphoryl type which are optionally substituted by one or more groups selected from the groups of the hydroxyl, mercapto, nitro, thiocyanato, azido, cyano, pentafluorosulphonyl, alkyl, aryl, haloalkyl, alkoxy, haloalkoxy, alkylthio, haloalkylthio, alkoxyalkyl, haloalkoxyalkyl, alkylthioalkyl, haloalkylthioalkyl, cyanoalkyl, cyanoalkoxy, cyanoalkylthio, alkylsulphinyl, haloalkylsulphinyl, alkylsulphonyl, haloalkylsulphonyl and alkoxy sulphonyl, cycloalkyl, alkenyl, alkinyl, alkenyloxy, alkinyloxy, alkenylthio, alkinylthio, amino, N-alkylamino, N,N-dialkylamino, acylamino, hydroxyl, alkoxy, carboxy, carbamoyl, N-alkylcarbamoyl, N,N-dialkylcarbamoyl, alkoxycarbonyl or acyl type.

Apart from the core, the dendrons and their terminal functions, the dendrimers employed in the compositions according to the invention contain internal cavities which inherently result from the fact that branchings which belong to the spatial structure of these dendrimers exist.

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These internal cavities can allow in particular various substances to be included in the centre of the tree-like structure of these dendrimers. However, the size and accessibility of these internal cavities limits the inclusion of these substances to only those molecules whose size and characteristics are compatible with them.

By way of example and purely by illustration, Figure (VIII) hereinbelow shows such a dendrimer.

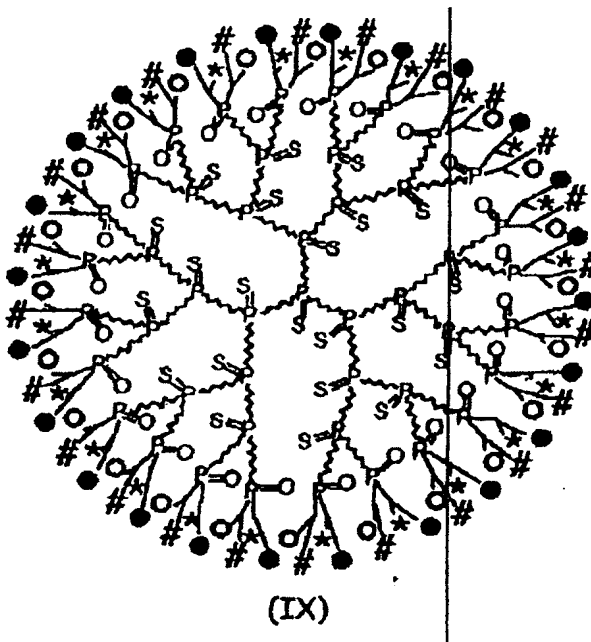


Moreover and because of the variety and number of terminal functions which the dendrimers employed in the compositions according to the invention may contain, these dendrimers may be referred to as being "equipped with a multiplicity of a plurality of functions".

Thus, the term "equipped with a multiplicity of a plurality of functions", means a dendrimer employed in the compositions according to the invention which has on its periphery a plurality of terminal functions with different chemical natures and where the plurality of these chemical functions is repeated owing to the multiplicity of the terminal functions.

A symbolic representation of such a dendrimer equipped with a multiplicity of a plurality of functions, more precisely with a multiplicity of four functions, which can be employed in the compositions according to the invention is shown hereinbelow in Figure (IX), where the symbols  $\bigcirc$ ,  $\bullet$ ,  $\star$  and  $\#$  represent terminal functions

of four different chemical natures and the broken lines show the dendrons of the dendrimer which is shown.



5

The gels formed by the dendrimers which can be used for the compositions according to the invention have the specific property of being able to contain, at the centre of their structure, two types of insertion  
10 volumes, for example of active substance:

- internal cavities which belong to the branched structure of the dendrimers themselves; and
- what are known as interstitial spaces, resulting from the three-dimensional structure of these gels  
15 which the said dendrimers can form.

In other words, the internal cavities are inside the dendrimers employed in the compositions according to the invention, while the interstitial spaces are  
20 outside the tree-like structure of these dendrimers.

These internal cavities of the dendrimers according to the compositions of the invention in general have dimensions of between 0.001 and 30 nm<sup>3</sup>, preferably  
25 between 0.01 and 10 nm<sup>3</sup>. The unit with which the size of

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these volumes can be estimated corresponds to the volume of a cube of lateral length 1 nm (nanometre).

What are known as the interstitial spaces of the gels which the dendrimers can form which can be used for the compositions according to the invention generally have dimensions of between 0.0005 and 50  $\mu\text{m}^3$ , preferably between 0.001 and 20  $\mu\text{m}^3$ . The unit with which the size of these volumes can be estimated corresponds to the volume of a cube of lateral length 1  $\mu\text{m}$  (micrometre).

The dendrimers employed in the compositions according to the invention generally amount in the compositions according to the invention to between 0.01 and 99.5%, preferably between 0.1 to 60%, by weight of the said compositions.

The invention furthermore relates to compositions which can be used in the fields of agriculture and/or public or domestic hygiene and which contain dendrimers according to the invention as well as one or more active substances in all or part of the interstitial spaces of these dendrimers, while the remainder is integrated in the centre of the internal cavities of these dendrimers.

Especially advantageous compositions according to the invention are those in which at least half of the active substance is present in the interstitial spaces of the gels formed by the dendrimers according to the invention.

This characteristic of compositions according to the invention, of being able to integrate part of the active substance in the centre of the spaces known as interstitial spaces, that is to say at the centre of the structure of the gels which the dendrimers employed can form, is particularly interesting since the size of this active substance makes it difficult, indeed

impossible, for them to be localized at the centre of the internal cavities of these dendrimers.

5 The invention thus relates to compositions such as described above, but also to compositions according to the invention which contain several active substances, in particular several active substances which can be used in the field of agriculture and/or public or domestic hygiene, in particular several pesticidal  
10 active substances and/or active substances which regulate the growth of plants and/or of insects.

The compositions according to the invention with which several of these active substances are associated or  
15 combined are of particular interest since these compositions allow several active substances with complementary ranges of action to be employed or else since these active substances are such that their association or combination can allow a substantial  
20 improvement of the activity of each of these active substances or else allow a reduction of the respective amount of each active substance used, the last-mentioned being particularly important for ecological reasons, as will readily be understood.

25 Thus, the compositions according to the invention can be particularly interesting due to the possibility of associating or combining several active substances, in particular the possibility of associating or combining  
30 one or more substances of the insecticide and/or acaricide and/or rodenticide and/or nematocide and/or insect repellent and/or pest repellent type with one or more attractants of these insects or pests.

35 In addition to one or more active substances as defined hereinabove and one or more dendrimers which can form a gel, the compositions according to the invention contain a mineral or organic liquid carrier.

- 30 -

For the purposes of the present invention, the term mineral or organic liquid carrier is most frequently understood as meaning a single solvent which is employed as well as an association of several solvents.

5 Such an association consists of a solvent and of one or more cosolvents which are miscible with each other or not.

Water and/or organic solvents may be used as solvents employed in the compositions according to the invention.

10

When water is used as solvent in the compositions according to the invention, its pH can equally well assume values which correspond to a basic environment as well as an acidic environment, for example depending on the type of dendrimer employed.

15

The organic solvents which may be employed for the compositions according to the invention are protic or aprotic organic solvents.

20

Among the organic solvents used for the compositions according to the invention, polar organic solvents are preferred, and such organic solvents are advantageously selected from among glycerol, ethanol, acetonitrile, tetrahydrofuran, dimethyl sulphoxide, N-methylpyrrolidone or cyclohexanone.

25

For the compositions according to the invention in which a solvent and one or more cosolvents are employed, the relative amounts of what are known as solvents and cosolvents vary within a solvent/cosolvent ratio of from 95/5 to 50/50.

30

In accordance with a particularly advantageous embodiment, the compositions according to the invention can release all or part of the active substance which can be used in particular in the fields of agriculture

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and/or public or domestic hygiene which they contain in a progressive and/or a controlled manner.

5 These compositions according to the invention can very advantageously release at least 50%, preferably at least 80%, of the active substance which can be used in particular in the fields of agriculture and/or public or domestic hygiene which they contain.

10 Preparation of compositions according to the invention

The present invention likewise relates to processes for the preparation of compositions according to the invention.

15

The processes for the preparation and formulation of the compositions according to the invention employ most frequently techniques conventionally used in the art of formulation, however, a process for the preparation of  
20 compositions according to the invention is given hereinbelow by way of example and for a better understanding of the present invention.

25 Unless otherwise specified, the amounts of different constituents used during these preparations are expressed as per cent by weight of the composition prepared.

30 To prepare such compositions, one therefore generally starts by mixing the dendrimer(s) which can form a gel in an amount which is most frequently between 0.01 and 99.5%, preferably between 0.1 and 60%, with the solvent or else the solvent/cosolvent mixture. Then the active substance(s) are added to the mixture prepared thus in  
35 amounts of between 0.5 and 99.99%, preferably between 5 and 70%. The additives and formulation adjuvants which are optionally employed in the compositions according to the invention can be added during one or the other of the steps described above; the skilled worker will

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know how to determine the best step and the useful amounts of these additives and adjuvants, these amounts advantageously being between 0 and 50%. After storage for a period of most frequently between a few hours and  
5 a few weeks, at a temperature which is generally between room temperature and approximately 80°C, preferably between 30 and 70°C, the mixture thus formed allows the compositions according to the invention to be obtained.

10

To prepare the compositions according to the present invention, the procedure is as follows: one or more active substances which can be used in the fields of agriculture and/or public or domestic hygiene, one or  
15 more dendrimers which can form a gel and a mineral or organic liquid carrier are mixed or solubilized, preferably while hot, and then this mixture is heated for 0.25 to 45 days at a temperature of approximately 30-65°C, preferably at a temperature of approximately  
20 35-40°C.

Pulverulent compositions which are useful in the fields of agriculture and/or public or domestic hygiene

25 Another aspect of the present invention relates to pulverulent compositions which can be used in the fields of agriculture and/or public or domestic hygiene and which, when mixed with a mineral or organic liquid carrier or solvent can reassume the form of  
30 compositions in gelled form, these compositions in gelled form being of the type of those described hereinabove.

The pulverulent compositions according to the invention  
35 can be obtained by the total or partial elimination of the solvent(s) from the compositions in gelled form according to the invention described hereinabove which contain, in addition to the solvent(s), one or more pesticidal active substances and/or active substances



which regulate the growth of plants and/or insects, a dendrimer according to the invention which can form a gel and optionally one or more adjuvants and/or formulation additives.

5

Thus, the pulverulent compositions according to the invention can contain, for example, anti-caking agents, colorants, thickeners, surfactants, antifoam compounds, detergents such as salts of alkaline earth metals, dispersants, alkalinizing agents such as bases, stickers, emulsifiers, oxidants such as free-radical scavengers or anti-hydroperoxide catalysts, corrosion inhibitors, attractants and/or food substances for the preparation of baits, in particular insecticidal baits.

15

More generally, the pulverulent compositions according to the invention can contain any additives which are used in the art of formulation and which are acceptable for uses in, for example, the fields of agriculture and/or public or domestic hygiene.

20

The active substances employed in the pulverulent compositions according to the invention are the active substances used for the formulation of compositions in gelled form according to the invention which have been described in detail hereinabove. Thus, active substances which may be mentioned among the said active substances employed in the pulverulent compositions according to the invention are all those which have been cited above as examples of active substances which the compositions in gelled form according to the invention may contain.

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30

The active substance(s) of the pulverulent compositions according to the invention are present in amounts of between 2 and 99.99%, preferably between 5 and 95%, by weight of these pulverulent compositions.

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Equally, the dendrimers employed in the pulverulent compositions according to the invention are the dendrimers which are employed for the compositions in gelled form according to the invention which have been  
5 described above.

In general, the main characteristic of these dendrimers is that they can form a gel as described above and can thus impart, to the pulverulent compositions according  
10 to the invention, their essential property of allowing the compositions in gelled form according to the invention to be reconstituted.

The dendrimer(s) which are useful for the pulverulent compositions according to the invention can be present  
15 in these pulverulent compositions in amounts of between 0.01 and 99.5%, preferably between 0.5 and 50% by weight of these pulverulent compositions.

It has thus been found that all or part of the solvent(s) can be removed from the compositions in gelled form according to the invention, thus allowing the preparation of pulverulent compositions according  
20 to the invention.

25 Techniques which are employed for the preparation of these pulverulent compositions according to the invention which may be mentioned are lyophilization or else atomization.

30 The purpose of lyophilization is to obtain pulverulent compositions according to the invention which are solid, loose, porous and characterized essentially by a very pronounced avidity for the solvent(s) which can be  
35 employed for the reconstitution of the compositions in gelled form according to the invention starting from these pulverulent compositions.

Lyophilization consists in extracting the solvent(s) which are present in the compositions in gelled form according to the invention by the interaction of vacuum techniques and freeze techniques, because a  
5 lyophilization cycle may comprise a plurality of phases, in particular a phase before freezing the composition to be lyophilized followed by a solvent elimination phase.

10 Drying by atomization of compositions in gelled form according to the invention can be carried out in the usual manner in any known apparatus, such as, for example, a spray tower in which spraying of such a composition in gelled form, which is carried out with a  
15 nozzle or turbine, is combined with a stream of hot gas.

The operating conditions generally depend on the nature of the solvent(s) to be eliminated and/or the nature of  
20 the dendrimer(s) according to the invention which is/are employed and/or on the heat sensitivity of the active substance(s) employed as well as the atomizer used; these conditions are generally such that the temperature of the whole composition according to the  
25 invention does not exceed 150°C, preferably 110°C, during drying.

The pulverulent compositions according to the invention are particularly advantageous because, when they are  
30 mixed with one or more suitable solvents, they can allow the reconstitution of compositions in gelled form according to the invention.

The solvent(s) used for admixing with the pulverulent  
35 compositions according to the invention can advantageously be selected from among water and/or the organic solvents.

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When water is employed as solvent which is added to the pulverulent compositions according to the invention, its pH can equally well assume values which correspond to a basic environment or values which correspond to an acidic environment, for example depending on the type of dendrimer employed.

The organic solvents which may be added to the pulverulent compositions according to the invention take the form of protic and/or aprotic organic solvents.

Among the organic solvents which may be added to the pulverulent compositions according to the invention, polar organic solvents are preferred, and such organic solvents are advantageously selected from among glycerol, ethanol, acetonitrile, tetrahydrofuran, dimethyl sulphoxide, N-methylpyrrolidone or cyclohexanone.

The pulverulent compositions according to the invention can not only allow the reconstitution of compositions in gelled form according to the invention, but are particularly advantageous because they can be stored over long periods without needing any care, while essentially retaining their characteristics.

In accordance with another advantageous embodiment, the pulverulent compositions according to the invention can be ground in order to obtain a particle size which is suitable for the intended use, in particular for facilitating spreading or else for improving the biological efficiency.

Moreover, these pulverulent compositions according to the invention can likewise be incorporated or employed in a large number of formulations. The said formulations can be in particular in liquid or solid form; thus, the following types may be mentioned among

these formulations: aerosol dispenser, bait (ready to use), bait concentrate, bait stock, capsule suspension, cold-fogging product, dusting powder, emulsifiable concentrate, emulsion of the aqueous type, emulsion of the oily/inverted type, encapsulated granules, fine granules, concentrated suspension for seed treatment, compressed gas, gas-generating product, grain bait, granular bait, granules, hot-fogging product, macrogranules, microgranules, oil-dispersible powder, oil-dilutable suspension concentrate, oil-miscible liquid, paste, rod for agropharmaceutical applications, plaque bait, powder for dry seed treatment, scrap bait, treated or coated seeds, smoke candle, smoke cartridge, smoke-generating product, smoke granules, smoke rodlet, smoke tablet, smoke tin, soluble concentrate, soluble powder, liquid for seed treatment, suspension concentrate (= flowable concentrate), tracking powder, ultra-low-volume liquid, ultra-low-volume suspension, vapour-releasing product, water-dispersible granules or tablets, wettable powder for slurry treatment, water-soluble granules or tablets, soluble powder for seed treatment, wettable powder.

In accordance with another embodiment, the pulverulent compositions according to the invention can be obtained by drying, followed by cutting, grinding, flaking or chopping gelled compositions according to the invention. In accordance with other advantageous embodiments, the pulverulent compositions according to the invention can take the form of coated tablets, a mass, aggregates in various sizes depending on the intended use, or else crystals, which can all be employed as such, in particular by spreading, dispersing or other suitable ways of application.

35

In accordance with another particularly advantageous embodiment, the pulverulent compositions according to the invention can release all or some of the active substance which they contain and which can be used in

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particular in the fields of agriculture and/or public or domestic hygiene in a progressive and/or controlled manner.

5 Even more advantageously, these pulverulent compositions according to the invention can release at least 50%, preferably at least 80%, of the active substance which they contain and which can be used in particular in the fields of agriculture and/or public  
10 or domestic hygiene.

### Dendrimers

The gels which can be formed by the dendrimers are  
15 colloids with an essentially continuous phase which give a gel-like viscous product; they may likewise take the form of a dispersed system comprising for example a high-molecular-weight compound or an aggregate of dendrimer molecules which are a subject matter of the  
20 invention in close association with a liquid.

As has already been mentioned hereinabove, the dendrimers are macromolecules which consist of a central part, namely the core, to which various  
25 branched chains, namely the dendrons, are attached.

These dendrimers most frequently have a tree-like structure, this structure comprising

- a core, which is most frequently composed of a  
30 polyfunctional chemical group and capable of being attached to several branched chains;
- branches, generally composed of linear or branched organic moieties which are attached between each other and to the core and which have a tree-like structure;
- 35 - chemical terminal functions, that is to say which form the outer end of these branches;
- internal cavities which result inherently from the branchings of these branches.

The organic core is thus the central part of dendrimers. In general, it consists of a chemical group, most frequently of an organic polyfunctional group which can be attached to a multiplicity of  
5 branched chains.

The core of dendrimers is likewise characterized by a multivalency which corresponds to the number of dendrons to which it can be attached.

10

As defined above, the organic core of dendrimers consists most frequently of a polyfunctional organochemical group and can be attached to a multiplicity of branched chains.

15

The said core can likewise be characterized by a multiple valency which corresponds to the number of dendrons to which it can be attached directly to give what is known as a first-generation dendrimer.

20

Preferably, the dendrimer core has a valency of between 2 and 20, preferably between 3 and 10. Thus, what are known as first-generation dendrimers can be attached to up to 20, preferably up to 10, dendrons.

25

Most frequently, the dendrimer core is composed of a more or less complex radical or chemical group; it may take the form of a hydrocarbon radical which generally contains 1 to 30 atoms and this hydrocarbon radical can  
30 be straight-chain, branched or cyclic, or even polycyclic, and/or saturated or unsaturated and/or substituted or unsubstituted.

The dendrimer core is usually composed of a hydrocarbon radical containing one or more hetero atoms, in  
35 particular oxygen, sulphur, nitrogen, phosphorus or else halogens, in particular chlorine. Optionally, and by way of preference, the dendrimer core contains up to

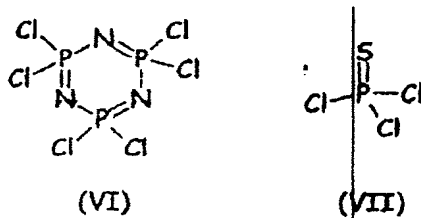
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100% (in terms of number of atoms) of these hetero atoms.

By way of examples of precursors of hetero-atom radicals which can be used as dendrimer core, hexachlorocyclotriphosphazene or else trichlorothiophosphane may be mentioned; the chemical structure of these two compounds is shown hereinbelow by formulae (VI) and (VII).

10

By precursors there are understood compounds which can precede the formation or preparation of radicals which can be used as dendrimer core.



15

The dendrimer dendrons are branched organic chains which are attached to the core. In general, the dendrons are series of these branched chains.

20

The said branched chains are usually composed of more or less complex hydrocarbon radicals, it likewise being possible for the hydrocarbon radicals to comprise a number of hetero atoms such as oxygen, sulphur, nitrogen, phosphorus or else halogens, in particular chlorine.

25

In general, the said dendrons are series of these branched chains; in other words, the dendrimers according to the invention most frequently have dendrons which are composed of branched chains containing chemical motifs which are partly identical or similar to each other.

30



The dendrimers can have a large number of dendrons and the number of these identical or similar chemical motifs varies greatly. Usually, the dendrimers have dendrons which are composed of a series of branched chains containing chemical motifs among which 10%, preferably 20%, of the total number of these chemical motifs are identical or similar. In other words, the dendrons of dendrimers are most frequently composed of chemical motifs of which 9/10, preferably 4/5, differ from each other.

These chemical motifs which the dendrons of dendrimers are composed of are most frequently chosen for example from among the groups of the alkyl, aryl, alkoxyalkyl, alkoxyaryl, alkylhydrazino, arylhydrazino, carboxy-alkylhydrazido and in particular carboxymethylhydrazido, cyanoalkyl, allyl, propargyl, halocycloalkyl, haloalkoxyalkyl, alkylthioalkyl, haloalkylthioalkyl, aminoalkyl, N-alkylaminoalkyl, N,N-dialkylaminoalkyl, acylaminoalkyl, arylalkyl, phenyliminoalkyl, iminoaryl, imidoalkyl, amidoaryl, phosphoralkyl, phosphoryl, thiophosphoryl, phosphoraminoalkyl, phosphoraminoaryl, phosphoriminoalkyl, phosphoriminoaryl, phosphorimidoalkyl, phosphorimidoaryl, hydrazinoalkyl, hydrazinoaryl, allylidenealkylhydrazino, allylidenearylhydrazino, epoxybenzylidene, dialkylphosphorimido, diarylphosphorimido, thioimido-phosphoryl, thio-N-alkylazophosphoryl or thio-N-arylazophosphoryl type which are optionally substituted by one or more groups selected from the groups of the hydroxyl, mercapto, nitro, thiocyanato, azido, cyano, pentafluorosulphonyl, alkyl, aryl, haloalkyl, alkoxy, haloalkoxy, alkylthio, haloalkylthio, alkoxyalkyl, haloalkoxyalkyl, alkylthioalkyl, haloalkylthioalkyl, cyanoalkyl, cyanoalkoxy, cyanoalkylthio, alkylsulphinyl, haloalkylsulphinyl, alkylsulphonyl, haloalkylsulphonyl and alkoxysulphonyl, cycloalkyl, alkenyl, alkynyl, alkenyloxy, alkynyloxy, alkenylthio, alkynylthio, amino, N-alkylamino, N,N-dialkylamino,

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acylamino, hydroxyl, alkoxy, carboxy, carbamoyl, N-alkylcarbamoyl, N,N-dialkylcarbamoyl, alkoxycarbonyl or acyl type.

5 The terminal functions of dendrimers are chemical functions at the ends of the dendrons of these dendrimers; among the very large number of chemical functions which can make up these terminal functions the ammonium, amidinium, pyridinium, guanidinium,  
10 carboxylate or else carboxylic acid functions may be mentioned by way of example. These terminal functions usually impart some of their characteristics to the dendrimers, in particular the possibility of very large numbers of individual reactions on the periphery.

15

The terminal functions of the dendrimers are attached to the ends of branched chains which make up the branches of these dendrimers, either directly or by means of an organic radical referred to as connecting  
20 member in the present context.

This connecting member of the dendrimers is most frequently composed of a hydrocarbon radical containing 2 to 50 carbon atoms, preferably 4 to 20 carbon atoms,  
25 it being possible for this radical to be saturated or unsaturated and/or straight-chain or branched and/or substituted or unsubstituted.

This connecting member can likewise be composed of a  
30 hydrocarbon radical as defined hereinabove and contain, in addition to carbon atoms, one or more hetero atoms, in particular oxygen, sulphur, nitrogen, phosphorus, halogens or any other element which can be used to impart, to the dendrimers which are the subject of the  
35 invention, the characteristics by which they are characterized, in particular their chemical reactivity.

Connecting members which can be used for the dendrimers and which may be mentioned are groups of the alkyl,

aryl, alkoxyalkyl, alkoxyaryl, alkylhydrazino, arylhydrazino, carboxyalkylhydrazido and in particular carboxymethylhydrazido, cyanoalkyl, allyl, propargyl, halocycloalkyl, haloalkoxyalkyl, alkylthioalkyl, haloalkylthioalkyl, aminoalkyl, N-alkylaminoalkyl, N,N-dialkylaminoalkyl, acylaminoalkyl, arylalkyl, phenyliminoalkyl, iminoaryl, imidoalkyl, amidoaryl, phosphoralkyl, phosphoryl, thiophosphoryl, phosphoraminoalkyl, phosphoraminoaryl, phosphoriminoalkyl, phosphoriminoaryl, phosphorimidoalkyl, phosphorimidoaryl, hydrazinoalkyl, hydrazinoaryl, allylidenealkylhydrazino, allylidenearylhydrazino, epoxybenzylidene, dialkylphosphorimido, diarylphosphorimido, thioimido-phosphoryl, thio-N-alkylazophosphoryl or thio-N-arylazophosphoryl type which are optionally substituted by one or more groups selected from the groups of the hydroxyl, mercapto, nitro, thiocyanato, azido, cyano, pentafluorosulphonyl, alkyl, aryl, haloalkyl, alkoxy, haloalkoxy, alkylthio, haloalkylthio, alkoxyalkyl, haloalkoxyalkyl, alkylthioalkyl, haloalkylthioalkyl, cyanoalkyl, cyanoalkoxy, cyanoalkylthio, alkylsulphinyl, haloalkylsulphinyl, alkylsulphonyl, haloalkylsulphonyl and alkoxysulphonyl, cycloalkyl, alkenyl, alkynyl, alkenyloxy, alkynyloxy, alkenylthio, alkynylthio, amino, N-alkylamino, N,N-dialkylamino, acylamino, hydroxyl, alkoxy, carboxy, carbamoyl, N-alkylcarbamoyl, N,N-dialkylcarbamoyl, alkoxycarbonyl or acyl type.

Apart from the core, the dendrons and their terminal functions, the dendrimers contain internal cavities which inherently result from the fact that branchings which belong to the spatial structure of these dendrimers exist.

35

These internal cavities can allow in particular various structures to be included in the centre of the tree-like structure of the dendrimers which are the subject of the invention. However, the size and accessibility

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of these internal cavities limits the inclusion of these substances to those molecules whose size and characteristics are compatible with them.

- 5 In general, the dimensions of these internal cavities of dendrimers are between 0.001 and 30 nm<sup>3</sup>, preferably between 0.001 and 10 nm<sup>3</sup>.

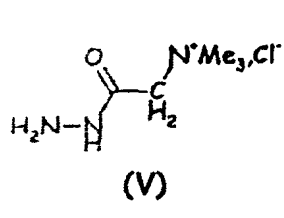
The dendrimers can take the form of neutral dendrimers  
10 or dendrimers of the ionic type, either of the anionic type or of the cationic type.

As neutral dendrimers, those whose terminal functions are mainly composed of groups of the carboxylic acid  
15 type and/or the phosphonic acid type and/or the sulphonic acid, sulphonate or sulphate type and/or the amine type may be mentioned.

As dendrimers of ionic type, those which can be  
20 mentioned advantageously are the dendrimers whose terminal functions consist essentially of groups selected from carboxylate and/or sulphonium and/or phosphonium and/or amidinium and/or guanidinium and/or ammonium groups, for example groups of the secondary,  
25 tertiary or quaternary ammonium type, most particularly groups of the pyridinium type.

Very particularly advantageous dendrimers which may be mentioned are those dendrimers whose terminal functions  
30 contain essentially groups of the N-hydrazinocarbonylmethyl-N,N,N-trialkylammonium type, among which N-hydrazinocarbonylmethyl-N,N,N-tri(n-propyl)ammonium chloride, also referred to as Girard PR reactant, or N-hydrazinocarbonylmethyl-N,N,N-trimethylammonium  
35 chloride, which is shown in Figure (V) hereinbelow and referred to as Girard T reactant, may be mentioned by way of example, or else N-hydrazinocarbonylmethyl-N,N,N-pyridinium chloride, also referred to as Girard P reactant, may be mentioned.

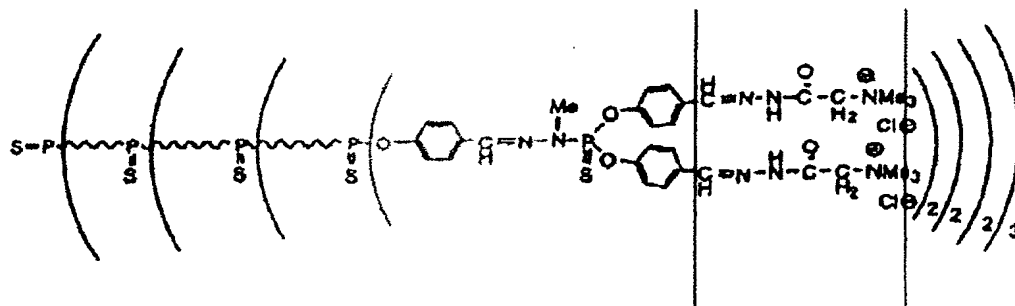
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Preferably, the dendrimers have bonds between atoms of the fifteenth column of the Periodic Table, this  
 5 fifteenth column being as defined above in the present context. More preferably, these dendrimers have bonds between phosphorus atoms and nitrogen atoms.

These bonds between atoms of the fifteenth column of  
 10 the Periodic Table may be present in the dendrimers in amounts of between a few units and several thousand, even several tens of thousands, owing to the large size which the said dendrimers may have; for example, the  
 15 number of these bonds can range between 2 and 80 000, preferably between 20 and 20 000.

Figure (VIII) shows a dendrimer by way of illustration only.



20

Apart from having the essential characteristic of being capable of forming gels, the dendrimers allow most frequently the formation of gels whose particular  
 25 characteristic is to contain two types of insertion volumes in their structure:

- internal cavities which belong to the branched structure of the dendrimers themselves; and

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- what are known as interstitial spaces, resulting from the three-dimensional structure of these gels which the dendrimers can form.

- 5 In other words, the internal cavities are inside the dendrimers, while the interstitial spaces are outside the tree-like structure of these dendrimers.

These internal cavities of dendrimers in general have  
10 dimensions of between 0.001 and 30 nm<sup>3</sup>, preferably between 0.01 and 10 nm<sup>3</sup>.

What are known as the interstitial spaces of the gels which the dendrimers can form generally have dimensions  
15 of between 0.0005 and 50 μm<sup>3</sup>, preferably between 0.001 and 20 μm<sup>3</sup>.

In accordance with another, particularly advantageous embodiment of the invention, the dendrimers can be used  
20 for encapsulating active substances, preferably for encapsulating active substances which are not or only sparingly soluble in water.

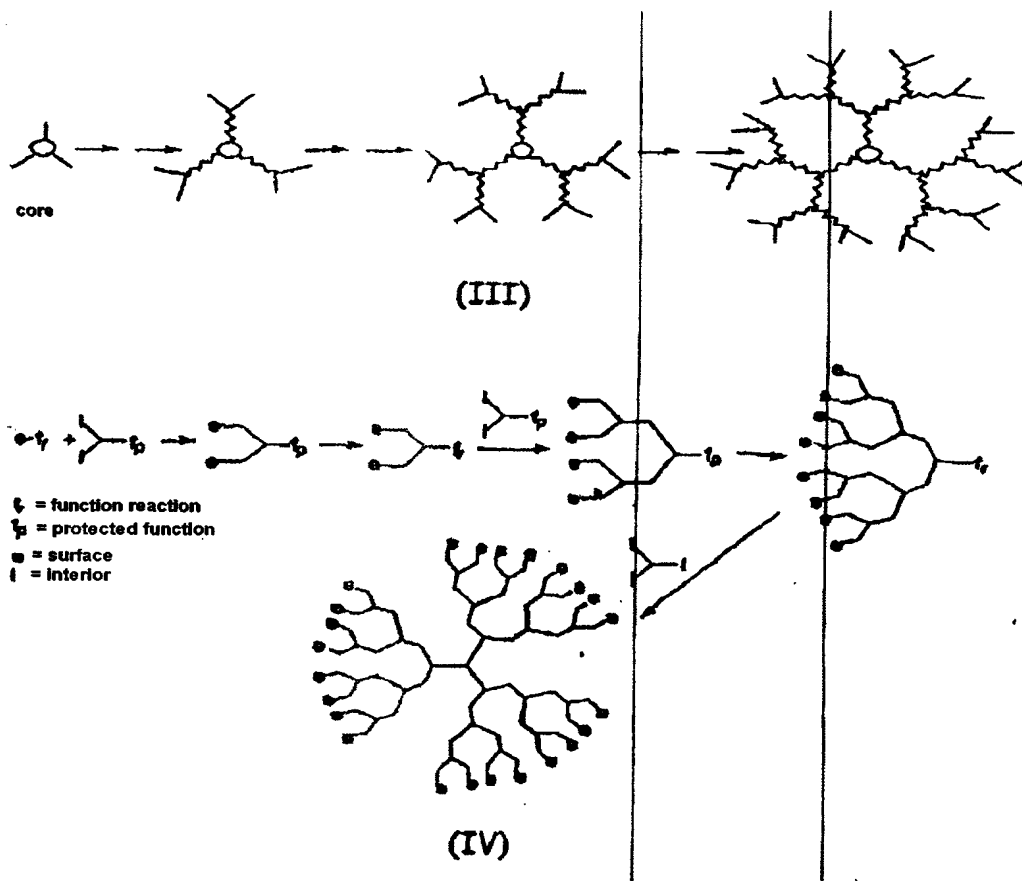
The term "not or only sparingly soluble in water"  
25 refers to substances whose solubility in water or in an essentially aqueous solvent makes these substances particularly difficult to use, or else substances whose useful active properties are substantially reduced owing to this difficulty, or impossibility, of  
30 solubilizing them in an effective manner.

#### Dendrimer preparation

To prepare these dendrimers and as has already been  
35 mentioned above in the present text, two types of synthetic methods, namely the divergent syntheses and the convergent syntheses may be mentioned for the preparation of dendrimers:

5 - in the divergent methods the synthesis progresses from the core towards the periphery by grafting increasing numbers of small molecules onto the surface of the dendrimer, which have a large number of chemical functions; such a synthetic pathway is shown in Scheme (III);

10 - in the convergent methods the synthesis progresses from the periphery towards the core by associating increasingly large molecules, which permanently have available a chemical function at the core, with each other; such a synthetic pathway is shown in Scheme (IV).



15

Preferably, what are called the divergent synthetic routes are employed for the preparation of dendrimers, that is to say the synthetic routes where the dendrimers grow from the core towards the periphery of these dendrimers, most frequently by reaction chains.

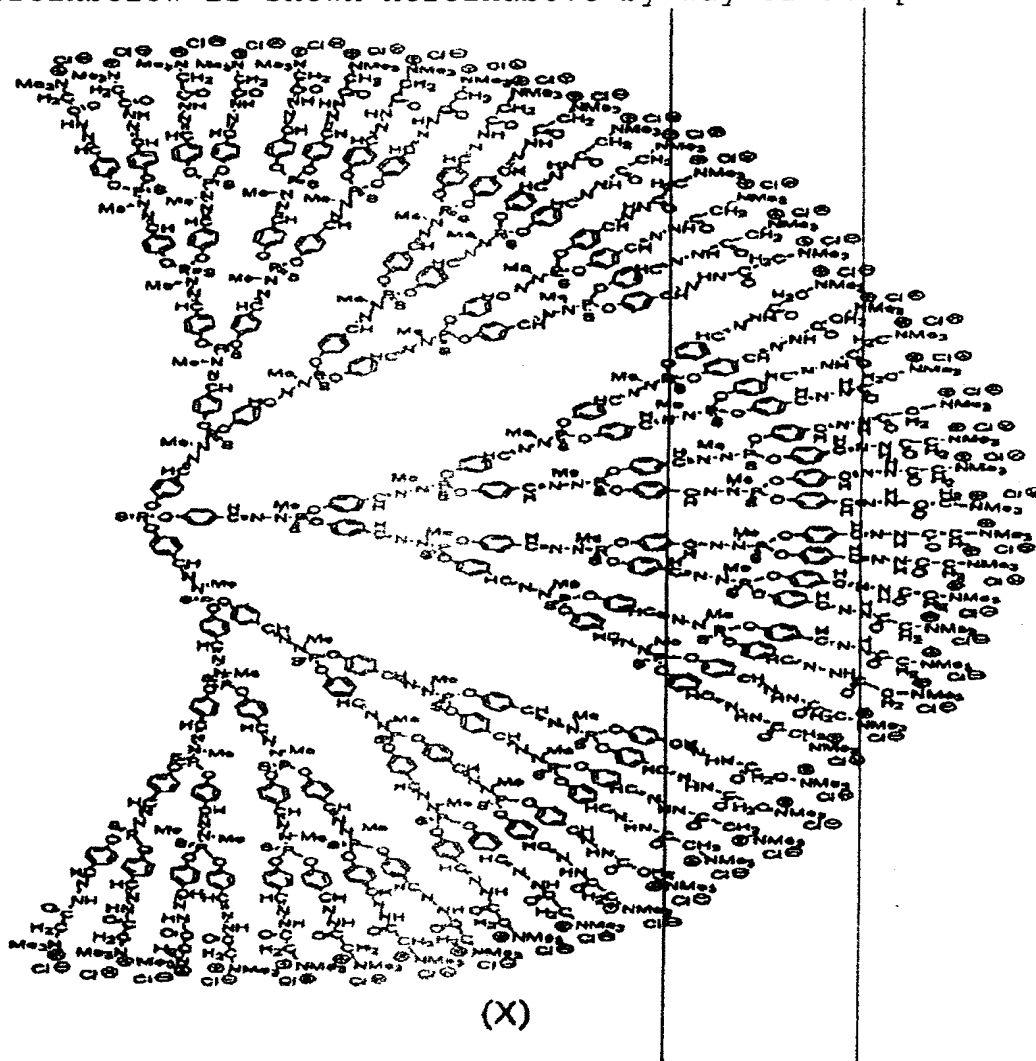
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Most preferably, the preparation of dendrimers is characterized by the fact that a dendrimer whose terminal functions are essentially composed of aldehyde-type functions with what is known as Girard reactant as described above, preferably a Girard T reactant, which has a trimethylammonium group, or a Girard PR reactant, which has a tri(n-propyl)ammonium group, or else what is known as a Girard P reactant, which has a pyridinium group.

10

A method of preparing the dendrimer shown in Figure (X) hereinbelow is shown hereinabove by way of example.



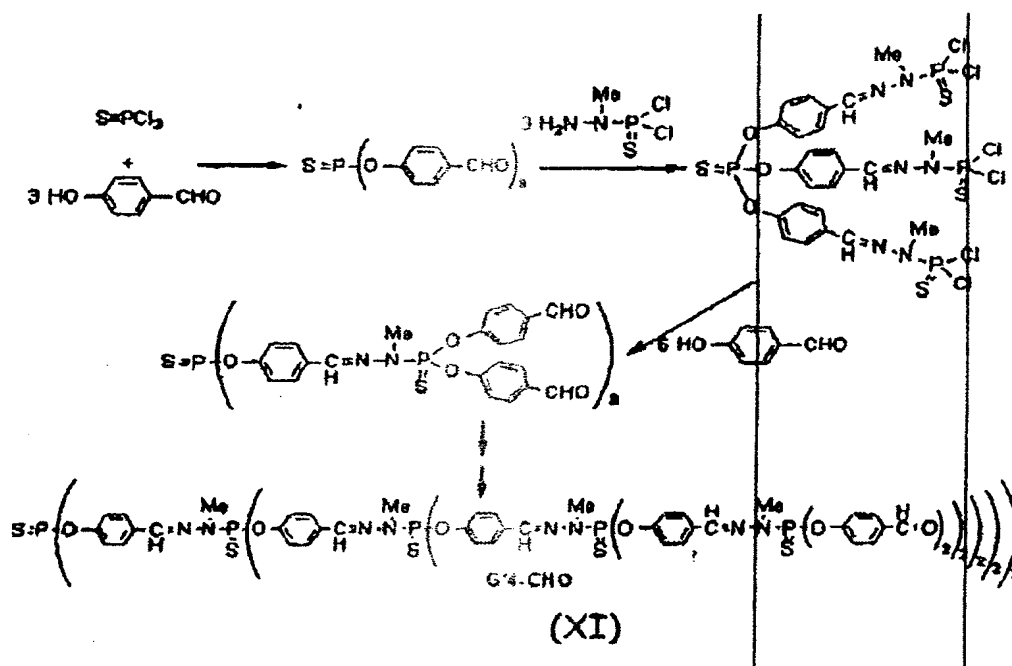
To aid the understanding of what follows, the dendrimer shown in Figure (X) whose terminal functions contain chemical radicals obtained from Girard T reactants is referred to as dendrimer G'-4-T.

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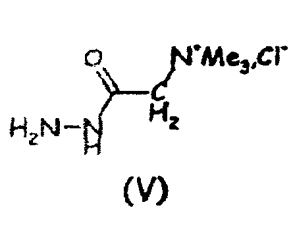


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To prepare this dendrimer G'-4-T, a dendrimer referred to as G'4-CHO whose terminal functions comprise essentially groups of the aldehyde type at the periphery, preferably where all these terminal functions are composed of groups of the aldehyde type at the periphery, are usually used; this dendrimer G'4-CHO can be prepared by referring to what is said in the work Les dendrimères which has been cited above in the present text. To prepare this dendrimer G'4-CHO, it is possible, for example, to follow the reaction scheme shown in Figure (XI) hereinbelow.



Then, this dendrimer G'4-CHO can be reacted in the presence of what is known as the Girard T reactant as described hereinabove in the present text, which is shown hereinbelow in Figure (V), to obtain the dendrimer known as G'-4-T.



- 50 -

Using a preparation method similar to the one described above for the preparation of dendrimer G'4-T, a dendrimer known as G'4-P, whose terminal functions contain chemical radicals obtained from Girard P reactants can be obtained.

The treatment and/or protection methods in which the compositions according to the invention which have been described in the present text are used, are likewise part of this invention. Preferred among the treatment methods are the treatment or protection methods which can be used in the fields of agriculture and/or public or domestic hygiene.

Treatment and/or protection methods which can be used in the field of agriculture, in particular for the treatment of crops

The methods according to the invention for the treatment or protection of crops according to the invention have the essential characteristic of including the step of employing an effective, non-phytotoxic amount of one or more compositions according to the invention.

By the term "effective, non-phytotoxic amount" there is understood for the purposes of the present text an amount of composition according to the invention which suffices for controlling and/or destroying and/or eradicating in particular diseases and/or fungi and/or harmful plants and/or harmful insects or animals which are present, or can appear, on the crops, as well as for controlling, in a satisfactory manner, the growth of these crops, while these crops do not suffer any phytotoxicity symptoms.

Such an amount can vary within fairly wide limits, in particular as a function of the cultures which are treated, the requirements, the type of disease to be

treated, the harmful insects and/or animals, the harmful plants to be controlled, destroyed or eradicated, the infestation level with these pests, the climatic and/or soil conditions, and the active  
5 substance(s) present in the composition(s) according to the invention which is/are employed.

The compositions according to the invention are most frequently used in amounts of between 1 g/ha and  
10 5 kg/ha.

The methods according to the invention for the treatment and/or protection of crops can in particular employ the compositions according to the invention  
15 which have previously been diluted or dispersed in a suitable amount of water.

Treatment methods which can be used in the field of public or domestic hygiene

20

As regards the treatment or protection methods according to the invention which can be used in public or domestic hygiene, these are primarily characterized in that one or more compositions according to the  
25 invention described further above are employed, in particular one or more of these compositions in gelled form.

These treatment methods which can be used in public or  
30 domestic hygiene employ effective quantities of the said compositions for controlling, destroying or eradicating the harmful insects and/or animals which are present, or can appear, but likewise effective quantities of compositions according to the invention  
35 containing one or more active substances which regulate the growth of these harmful insects and/or animals.

These quantities can vary as a function of the degree of infestation with these harmful insects and/or

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animals to be controlled, destroyed or eradicated or else as a function of the climatic conditions or else as a function of the pesticidal active substance and/or growth-regulatory active substance employed. Amounts of composition according to the invention, in particular in the form of baits, in the order of from 0.1 to 200 g/m<sup>2</sup> are generally suitable.

The various treatment and/or protection methods according to the invention which have been described in which a gelled composition according to the invention is employed as well as those in which a pulverulent composition is used can advantageously employ these compositions in a number of forms, in particular in ground, chopped, cut-out, cut up, crushed, flattened, compressed, pressed, pounded, rolled, pulverized, milled, crushed, broken up, crumbled, dispersed, cut, divided, segmented, sliced or fractionated form.

Examples for allowing a better illustration of various aspects of the present invention are given hereinbelow.

Examples 1 and 2 illustrate methods for the preparation of compositions according to the invention, while Example 3 allows the aspect of the present invention in relation to the preparation of the dendrimers to which the invention relates to be illustrated.

Example 1:

30

To prepare a composition according to the invention, the following procedure is followed: to 724 g of water there are added 35 g of dendrimer of formula (X) referred to as G'4-T, 50 g of propylene glycol as antifreeze agent, 5 g of a wetting agent of the ethoxylated polyalcohol type and 6 g of an antifoam of the silicone oil type. 200 g of fenamidone, a fungicidal active substance with the chemical name (4-S)-4-methyl-2-methylthio-4-phenyl-1-phenylamino-2-

imidazolin-5-one, is dispersed in the resulting solution. Then, 25 g of a thickener of the silico-aluminate type are added. After the above-prepared mixture has been stored for 14 days at 54°C, a composition according to the invention is obtained.

#### Example 2:

The preparation method of Example 1 is followed, except that the 200 g of fungicidal active substance are replaced by 200 g of an insecticidal active substance, namely fipronil, with the chemical name 5-amino-3-cyano-1-(2,6-dichloro-4-trifluoromethyl)phenyl-4-trifluoromethylsulphinyldipyrrole, and that the 35 g of dendrimer G'4-T are replaced by 35 g of the dendrimer G'4-P as described above, whose terminal functions contain essentially radicals obtained from what are known as Girard P reactants, which have pyridinium groups. A composition in gelled form according to the invention is obtained which, when applied at approximately 0.1 g of active substance per 100 m<sup>2</sup> surface to be protected, constitutes an effective bait against cockroaches, in particular of the type *Blattella germanica*.

#### Example 3:

This example should provide a particular illustration of the aspect of the present invention which relates to the preparation of a composition according to the invention.

To a known formulation (200 g/l fipronil as insecticidal active substance, 400 g/l refined maize oil, 50 g/l propylene glycol as antifreeze agent, 13 g/l of an emulsifier, 25 g/l of a dispersant, 5 g/l of a wetting agent, 8 g/l of another wetting agent, 5 g/l of an antifoam, 344 g/l water as liquid carrier) of the flowable concentrate type comprising 200 g/l fipronil as active substance, 1.8% by weight of

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dendrimer G'4-P are added at a temperature of approximately 45°C.

The mixture obtained is subsequently placed into an oven at a temperature of approximately 60-65°C.

- 5 After two days, a composition according to the invention is obtained which is in the form of a dryable gel.

Example 4:

10

- To prepare the dendrimer G'4-T which is shown in Figure (X), the following procedure can be followed: to 10 g of dendrimer G'4-CHO, which are dissolved in 190 ml of tetrahydrofuran, there are added 100 ml of an  
15 aqueous solution containing 5.23 g of what is known as Girard T reactant. The reaction medium thus obtained is stirred for approximately 15 hours at room temperature. Thereafter, the reaction mixture is heated for approximately 4 days at 35°C. Then, the solvents are  
20 removed from the reaction medium and the solid thus obtained is washed with 300 ml of tetrahydrofuran, with stirring. The dendrimer G'4-T is thus obtained in the form of a white powder which is subsequently dried. The overall yield of the present preparation method is  
25 quantitative.